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TC 1700

Appl. No.	:	08/970,066	Confirmation No.: 2141
Applicant	:	P. K. Dhal et al.	
Filed	:	November 13, 1997	
Title	:	HOLOGRAPHIC MEDIUM AND PROCESS FOR USE THEREOF	
TC/A.U.	:	1756	
Examiner	:	M. J. Angebranndt	
Docket No.	:	8232-CPA	
Customer No.	:	20349	

Affidavit Under 37 CFR § 1.132

Commonwealth of Massachusetts)

                         : ss.

County of Middlesex   )

Waltham, Massachusetts 02451
August 4, 2003

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, David A. Waldman, being duly sworn, hereby depose and say that I am a citizen of the United States of America currently residing at 31 Mitchell Road, County of Middlesex, Commonwealth of Massachusetts.

That I am an applicant named in the above-identified application for Letters Patent which has claims directed to volume holographic recording media.

That I received the degree of Doctor of Philosophy in Polymer Science and Engineering from the University of Massachusetts-Amherst in 1990.

That I have worked in the field of holography since 1991 to the present.

That the following experiments were conducted:

I. The refractive indices of liquid monomers and the solid polymerized film of the monomers were measured for a difunctional epoxy monomer, a trifunctional epoxy monomer and a tetrafunctional epoxy monomer, each of the three monomers having the same chemical structure for the epoxy grouping.

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The difunctional- trifunctional- and polyfunctional- monomers are specifically described in patent application serial no. 08/970,066, filed November 13, 1997. The chemical structures of these three compounds are shown in Exhibit A, attached hereto and made a part of this Affidavit. Since the experimental measurements show that the optical dispersion is unchanged, then the change in refractive index, between the liquid monomer and the respective solid polymerized film of the monomer, is a direct measurement of the densification that occurs as a consequence of the polymerization. The densification correlates with the volume change (i.e. shrinkage) caused by the polymerization. A temperature controlled Bausch & Lomb Abbe-3L Refractometer was used to obtain all measurements of refractive index.

Experimental

Into each of three 1-dram glass vials was weighed Rhodorsil PI-2074 (5 mg, 1 wt.% photoacid generator "PAG"). The difunctional epoxy compound, in the amount of 500 mg, was added to one vial and the PAG was dissolved in the liquid compound with brief gentle warming and mixing with a Vortex-Genie Mixer. The trifunctional epoxy compound (alkylated trimer), in the amount of 500 mg, was added to the second vial, and the PAG was dissolved in the liquid compound with brief gentle warming and mixing. The tetrafunctional epoxy compound (C0 tetramer), in the amount of 500 mg, was added to the third vial, and the PAG was dissolved in the liquid compound with brief gentle warming and vortex mixing followed by wrapping the vial in aluminum foil to exclude light and rotating it on a rotary evaporator at atmospheric pressure and room temperature for about 2 hours.

Three sandwiches were prepared from the three solutions as follows: each of the resulting clear, colorless solutions was transferred by pipet into the gap between two 25 x 75 x 1 mm glass microscope slides spaced apart with two thicknesses of Scotch Magic tape (spacing ~100μ) and slightly offset (~4 mm) to aid in filling. The slides were then carefully squared up, each filled sandwich was set directly under the bell housing of a Normark Norlite 400 xenon flash lamp set at full aperture and highest power (300 W), and each monomer solution was cured with the number of flashes per side of the sandwich as shown in Tables 1-3. After each group of

exposures, the refractive index of the sandwiched film was measured by placing the sandwich on the prism of a Bausch & Lomb Abbe-3L Refractometer with a drop of Dow Corning 705 fluid (n_D^{20} = 1.58) as the contact liquid. When the refractive index of the polymer was no longer increasing, each sandwich was carefully pried apart with a razor blade to reveal a clear, colorless freestanding solid film. Each freestanding solid film was then further exposed to UV radiation from the Normark Norlite 400 flash lamp to ensure complete curing until no further change in refractive index was measureable to the accuracy limit of the Refractometer (fourth decimal place). Refractive indices of the freestanding films were measured by carefully pressing each film onto the Abbe refractometer prism without any contact liquid.

Table 1   Difunctional Epoxy Curing Data

n_D^{20}	# of flashes of Xenon lamp	Format
1.4772		Pure DEDS monomer
1.4778		Monomer solution with 1% PAG
1.4972	10 per side	Sandwich
1.4975	10 per side additional	Sandwich
1.4988	20 per side of free film	Freestanding film
1.4988	10 per side	Freestanding film

Table 2   Trifunctional Epoxy (Alkylated Trimer) Curing Data

n_D^{20}	# of flashes	Format
1.4688		Pure alkylated Trimer monomer
1.4695		Monomer solution with 1% PAG
1.4805	10	Sandwich
1.4832	10 additional	Sandwich
1.4837	10 additional	Sandwich
1.4845	10 to free film	Freestanding film
1.4848	10 additional	Freestanding film
1.4855	10 per side additional	Freestanding film

Table 3   Trifunctional Epoxy (C0 Tetramer) Curing Data

n_D^{20}	# of flashes	format
1.4796		pure C0 Tetramer monomer
1.4802		monomer solution with 1% PAG
1.4860	20	sandwich
1.4915	10 per side additional	sandwich
1.4940	0 additional	freestanding film
1.4945	10 per side	freestanding film
1.4947	10 per side + 15 minute rest	freestanding film

All z values (compensator dial readings for Abbe-3L prism #555) for the three monomers, the monomer solutions, and their respective polymer films were 18.5, which signifies that the optical dispersion of the liquid monomers and the corresponding polymerized films were essentially the same. Therefore, refractive index differences between each of these liquid monomers and the respective polymer films are due to changes in density without contribution from chromophore changes. With n_p = refractive index of the polymer film and n_m = refractive index of the monomer solution, the change in refractive index in converting each monomer to polymer was calculated from the standard formula, $\Delta n = (n_p/n_m) - 1$. The results are shown in Table 4.

Table 4 Δn Data for Difunctional and Multifunctional Epoxy Compounds
Comprising Ethyl Cyclohexeneoxide Grouping

Monomer	n_p	n_m	Δn
DEDS	1.4988	1.4778	+1.42%
Alkylated Trimer	1.4855	1.4695	+1.09%
C0 Tetramer	1.4947	1.4802	+0.98%

The decrease in Δn, for polymerization of the multifunctional epoxy compounds versus the difunctional compound, is $(\Delta n_{difunct}/\Delta n_{trifunct})$ -1 = 30.3% and $(\Delta n_{difunct}/\Delta n_{tetrafunct})$ -1 = 44.9%, respectively, for the trifunctional and tetrafunctional epoxy compounds. The decrease in Δn, shown for the multifunctional epoxide compounds versus the difunctional epoxy compound, represents a substantial

diminution that corresponds to a substantial decline in densification and thus reduction in volume shrinkage for the multifunctional epoxy compounds. Accordingly, when the multifunctional epoxy compounds are substituted for difunctional epoxy compound in a formulation used for holographic recording, then the shrinkage that occurs during the polymerization required for said holographic recording is diminished. The relationship between volume change of a material, measured by dilatometry, and refractive index change, measured as above, is typically about 3 to 1 for similar siloxy silane epoxy compounds.

II. Stable volume holographic image formation was measured for a prior art composition including a difunctional epoxide monomer and two compositions according to the invention which include both a difunctional epoxide monomer and a polyfunctional epoxide monomer.

Experimental

Holographic recording of unslanted plane-wave diffraction gratings was carried out by exposing coatings of candidate recording materials to a plane wave interference pattern constructed using two spatially filtered and collimated beam paths of s-polarized coherent light from an Ar^+ laser operating at 514.5 nm. For both beam paths, the incident semiangle ,θ, $= \pm 24.80°$ from the normal to the surface of the recording material and equal power densities ($\pm 1\%$) were used. Power density of each beam in mW/cm^2 is determined by placing a 1 cm^2 aperture directly in front of a Newport 818SL photodiode detector that is positioned at normal incidence to the beam path in close proximity to the sample holder. For purposes of calculating exposure fluence during holographic recording, in mJ/cm^2, the measured incident value of power density is reduced by the factor $\cos\theta$ of the measured interbeam angle to account for the angle related beam spreading at the plane of the recording material. The value of recording fluence for a holographic recording exposure is then the summation of the angle adjusted power density of the two beampaths multiplied by the length of the exposure in seconds. A beam expanded and collimated HeNe laser, emitting s-polarized coherent light at 632.8 nm with an incident power of 50 microwatts, was used to probe the real time development of refractive index

modulation, and thus holographic activity, by reconstructing the first order diffraction of the developing hologram both during exposure and following holographic imaging. The recording material does not exhibit holographic sensitivity to light from the HeNe laser at the aforementioned stated conditions. The kinetics of hologram formation is thus monitored real time without perturbing the hologram development itself. The rise time in detected intensity after the Newport mechanical shutter, model 846HP, is pulsed via a serial interface to open the imaging beam paths from the Ar^+ laser was shown to be less than about 10 milliseconds.

A 75/25 (monomer/binder weight % ratio) formulation consisting of (1) a fluid polysiloxane binder, poly (methylphenylsiloxane), known as Dow Corning 710 **(IA)** and which was stored over 4Å molecular sieve, (2) a di(cyclohexene oxide siloxane) monomer, GE Silicone 479-1893 **(IIA)** (neat), and (3) the photoinitiation system consisting of the 4, N-octyloxyphenyl phenyl hexafluoroantinomate iodonium salt **(IIIA)** and (5,12 - Bis(phenylethynyl)naphthacene) photosensitizer **(IV)** in the amounts of 5 % and 0.05 % by weight, respectively, was prepared and thoroughly degassed with argon to remove solvent that was used for dissolution of **IIIA** and **IV**, and is referred to as a Type I formulation.

A 75/25 (monomer/binder weight % ratio) formulation consisting of (1) a fluid polysiloxane binder, poly (methylphenylsiloxane), known as Dow Corning 710 **(IA)** and which was stored over 4Å molecular sieve, (2) a mixture of di(cyclohexene oxide siloxane) monomer, GE Silicone 479-1893 **(IIA)** (neat), and an akylated trifunctional epoxide; methyltris[dimethylsiloxy,2-(3{7-oxabicyclo[4.1.0]heptyl}) ethyl] silane **(IIB)** in a 3:1 mole ratio, and (3) the photoinitiation system consisting of the 4, N-octyloxyphenyl phenyl hexafluoroantinomate iodonium salt **(IIIA)** and (5,12 - Bis(phenylethynyl) naphthacene) photosensitizer **(IV)** in the amounts of 5 % and 0.05 % by weight, respectively, was prepared and thoroughly degassed with argon to remove solvent that was used for dissolution of **IIIA** and **IV**, and is referred to as a Type II formulation.

A 75/25 (monomer/binder weight % ratio) formulation consisting of (1) a fluid polysiloxane binder, poly (methylphenylsiloxane), known as Dow Corning 710 **(IA)** and which was stored over 4Å molecular sieve, (2) a mixture of di(cyclohexene oxide

siloxane) monomer, GE Silicone 479-1893 **(IIA)** (neat), and a tetrafunctional epoxide; tetrakis[dimethylsiloxy, 2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl] silane. **(IIC)** in a 1:1 mole ratio, and (3) the photoinitiation system consisting of the 4, N-octyloxyphenyl phenyl hexafluoroantinomate iodonium salt **(IIIA)** and (5,12 - Bis(phenylethynyl) naphthacene) photosensitizer **(IV)** in the amounts of 6.1 % and 0.1 % by weight, respectively, was prepared and thoroughly degassed with argon to remove solvent that was used for dissolution of **IIIA** and **IV**, and is referred to as a Type III formulation.

Glass substrates used to prepare the coating were float glass that was cleaned by submersion in KOH/isopropoanol for a minimum of 1 hour, followed by rinse with copious amounts of distilled water and final drying at 110°C for at least 1 hour. The coating was prepared in an enclosed box with iris port entry, said box being continuously purged with nitrogen flow from a source of boiled off liquid nitrogen. The coating of the formulation between said cleaned and dried glass substrates was effected by use of standard capillary flow methods.

Results

Figure 1 shows the intensity of 1° diffraction versus time during and after holographic recording for a 100 μm thick coating prepared from the Type I formulation. A six second continuous holographic recording exposure was carried out with an incident irradiance of about 9.3 mW/cm^2 starting at time t = 0 seconds. The total exposure fluence for this recording = 55.8 mJ/cm^2. The time for observation of stable 1° diffraction was about 2.8 seconds, which corresponds to a recording fluence of about ~ 26 mJ/cm^2 for the threshold recording energy.

In Figures 2 and 3 are shown the intensity of 1° diffraction versus time during and after holographic recording for a 100 μm thick coating prepared from the Type II formulation. An eight second continuous holographic recording exposure was carried out with an incident irradiance of about 5.1 mW/cm^2 starting at time t = 0 seconds. The total exposure fluence for this recording = 40.8 mJ/cm^2. The time for observation of stable 1° diffraction was about 1.94 seconds, which corresponds to a recording fluence of about ~ 9.9 mJ/cm^2 for the threshold recording energy.

In Figure 4 is shown the intensity of 1° diffraction versus time during and after holographic recording for a 100 μm thick coating prepared from the Type III formulation. A five second continuous holographic recording exposure was carried out with an incident irradiance of about 9.3 mW/cm^2 starting at time t = 0 seconds. The total exposure fluence for this recording = 46.5 mJ/cm^2. The time for observation of stable 1° diffraction was less than about 0.9 seconds, which corresponds to a recording fluence of less than about ~ 8.4 mJ/cm^2 for the threshold recording energy.

A significant diminution in the threshold energy requirement for observation of stable holographic activity occurs when the difunctional epoxide monomer is partially replaced in the holographic recording formulation with a trifunctional or tetrafunctional epoxide monomer. Use of multifunctional monomers or oligomers to promote rapid network formation via crosslinking reactions within regions of constructive interference provides a means of expeditiously attaining an effective degree of polymerization that crosses over into the entanglement regime where viscosity scales with molecular weight to at least the 3.4 power. In a dense solution the frictional coefficient of a polymer chain is proportional to the contour length of the chain, but is inversely proportional to the diffusion coefficient of the chain. In the entanglement molecular weight regime the disengagement time for a chain to leave its configurational constraints will thus scale with the 3rd power of the contour length. In this manner chain extension achieved with the combination of difunctional and multifunctional epoxides will be more competitive with diffusion processes that act to destabilize the initial stages of hologram formation. This advantage is particularly important when recording multiplexed binary data page holograms, such as for data storage applications. In such cases the diffraction efficiency of each multiplexed data page, where hundreds of such data page holograms are multiplexed in the same volume element of the recording material, is typically about 10^{-4} %. It is desirable, therefore, that the recording fluence necessary to record said data page holograms be as low as possible so that the holograms can be recorded as rapidly as possible and be stable for a defined recording power density of the system.
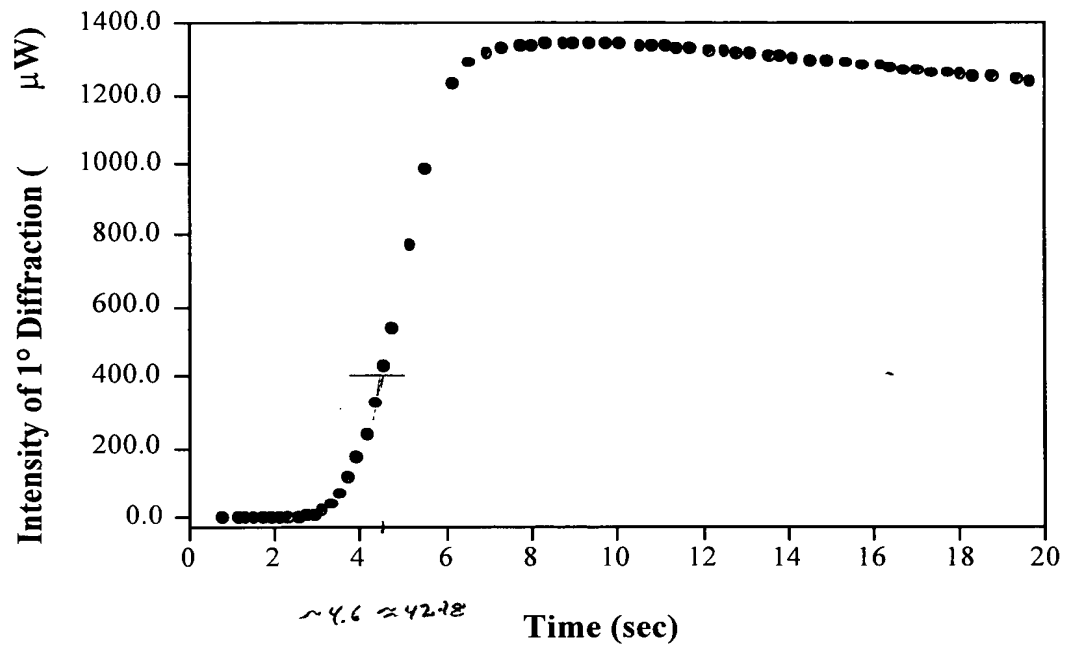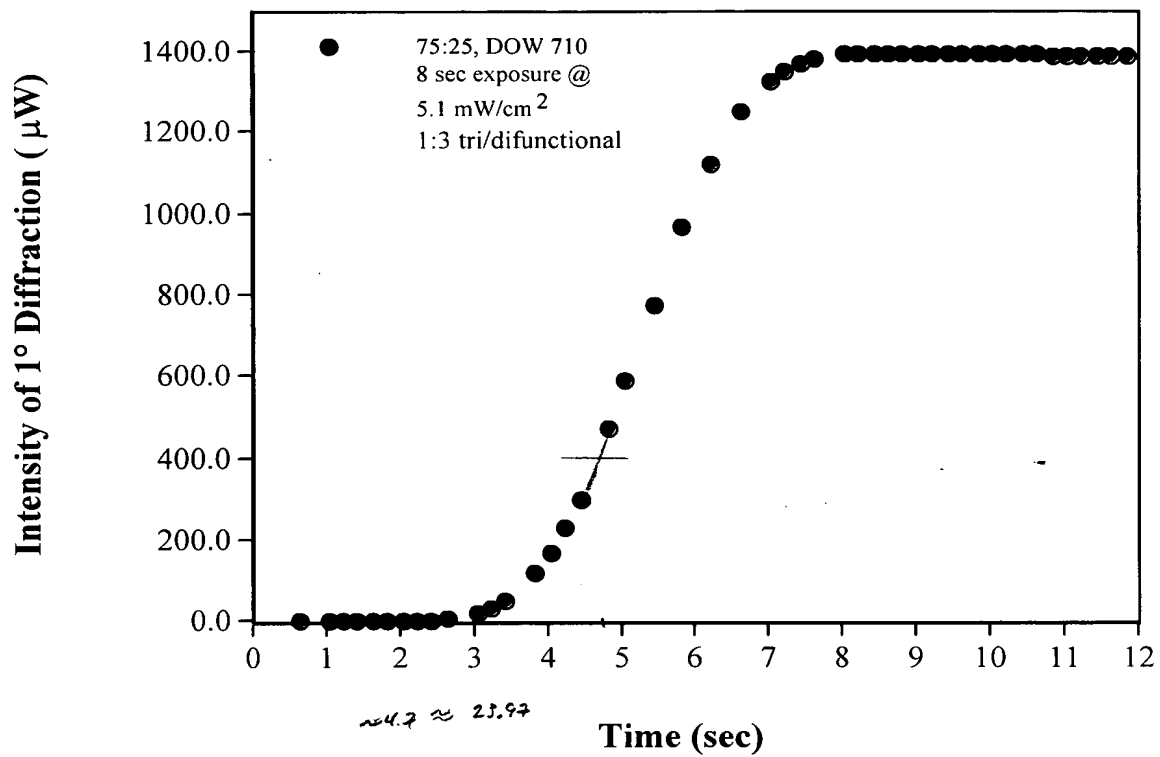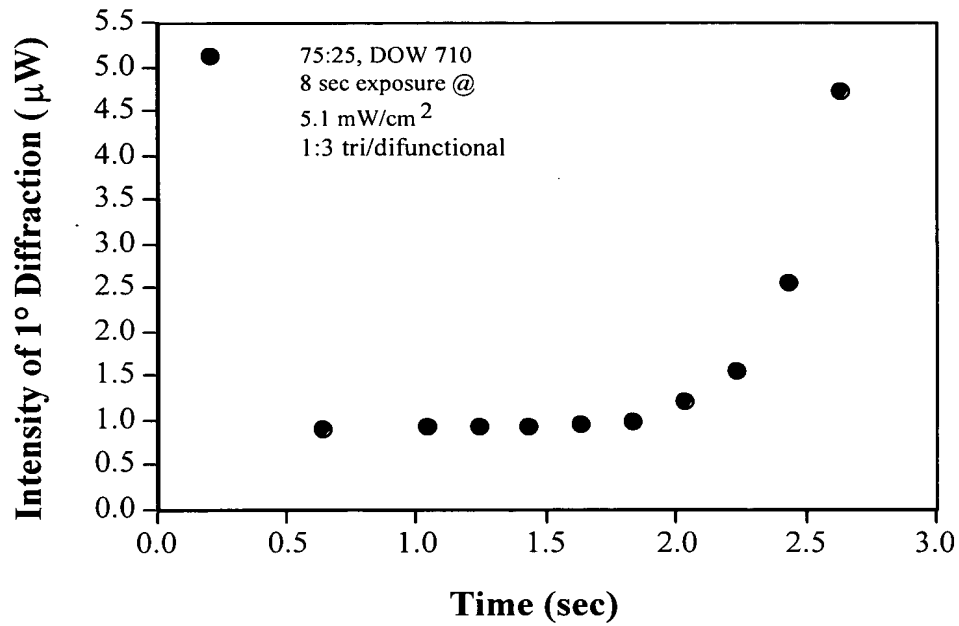
-8-

Figure 1. Intensity of 1° diffraction in μW, from measurements made with probe beam of HeNe Laser (632.8 nm), versus time in seconds during hologram development in 100 μm film of Type I formulation for a exposure time of t=6 seconds. Irradiance with Ar^+ laser (514.5 nm) = 55.8 mJ/cm^2 starting at time = 0 seconds.
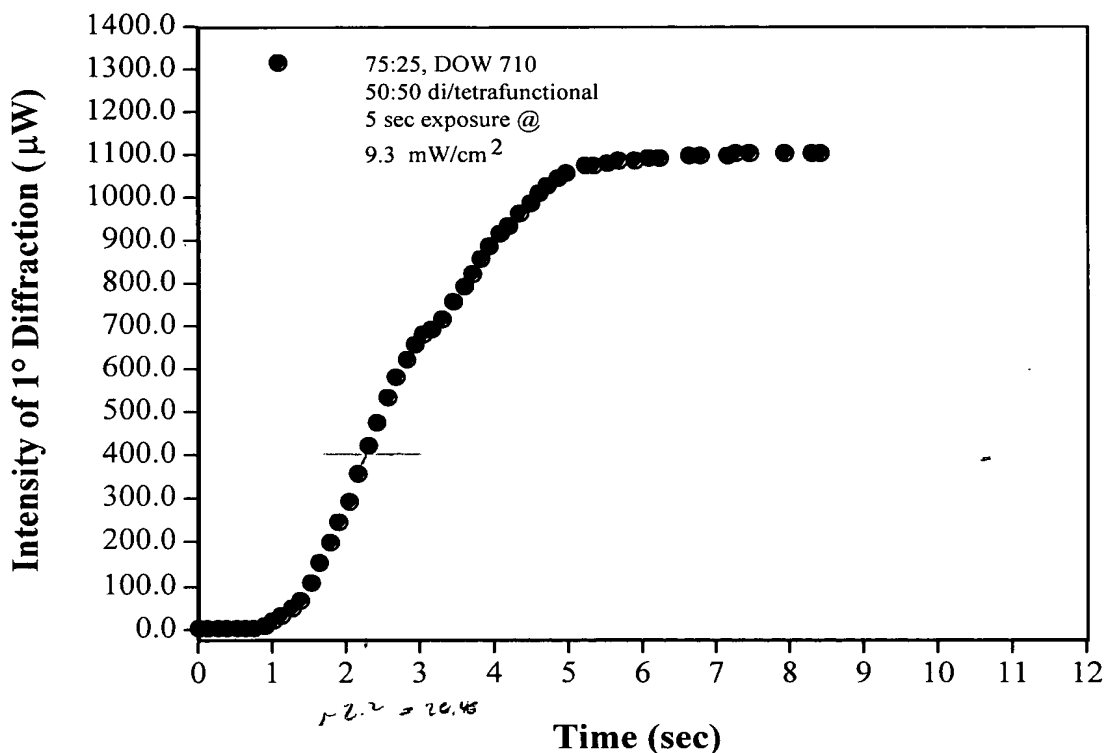
Figure 2.   Intensity of 1° diffraction in μW, from measurements made with probe beam of HeNe Laser (632.8 nm), versus time in seconds during hologram development in 100 μm film of Type II formulation for a exposure time of t=8 seconds. Irradiance with Ar^+ laser (514.5 nm) = 40.8 mJ/cm^2 starting at time = 0 seconds..

Figure 3. Intensity of 1° diffraction in μW, from measurements made with probe beam of HeNe Laser (632.8 nm), versus time in seconds during hologram development in 100 μm film of Type II formulation for a exposure time of t=8 seconds. Irradiance with Ar^+ laser (514.5 nm) = 40.8 mJ/cm^2 starting at time = 0 seconds. Data for first 3 seconds of holographic exposure
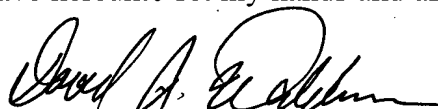
Figure 4. Intensity of 1° diffraction in μW, from measurements made with probe beam of HeNe Laser (632.8 nm), versus time in seconds during hologram development in 100 μm film of Type III formulation for a exposure time of t=5 seconds. Irradiance with Ar^+ laser (514.5 nm) = 46.5 mJ/cm^2 starting at time = 0 seconds.

IN WITNESS WHEREOF, I have hereunto set my hands and affixed my seal, this 4th day of August 2003.

David A. Waldman

Commonwealth of Massachusetts)
                                     : ss.
County of Middlesex)

On this 4th day of August 2003, before me, the subscriber, personally came David A. Waldman, to me known and known to me to be the same person described in and who executed the foregoing instrument, and duly acknowledged to me that he executed the same as his free act and deed.
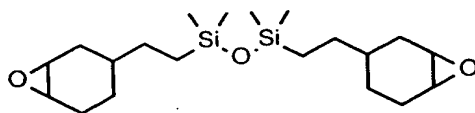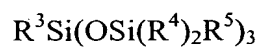
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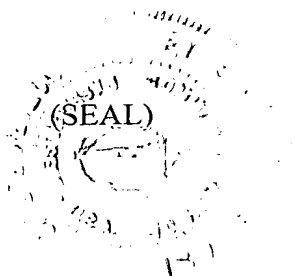
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EXHIBIT A

DIFUNCTIONAL EPOXIDE MONOMER

TRIFUNCTIONAL EPOXIDE MONOMER

$$R^3Si(OSi(R^4)_2R^5)_3$$
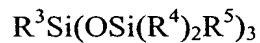
where each R^3 is methyl,

each R^4 is methyl and

each R^5 is 2-(3,4-epoxycyclohexyl)ethyl

TETRAFUNCTIONAL EPOXIDE MONOMER

$$R^3Si(OSi(R^4)_2R^5)_3$$

where each R^3 is (OSi(R^4)$_2$$R^5$,

each R^4 is methyl and

each R^5 is 2-(3,4-epoxycyclohexyl)ethyl